CLAIMS:

We claim:

1. A polymerization process comprising combining ethylene, at least one C₄ to C₁₂ α-olefin and a catalyst system comprising a polymerization catalyst and an activator; wherein the activator comprises a heterocyclic compound, which may be substituted or unsubstituted, in combination with an aluminum containing compound; wherein the aluminum containing compound is an alumoxane or an alkylaluminum compound represented by the formula AlR₃ wherein each R is independently a substituted or unsubstituted alkyl group.

- 2. The process of claim 1, further comprising a support material.
- 3. The process of claim 1, wherein the heterocyclic compound is selected from the group consisting of pyrroles, imidazoles, pyrazoles, pyrrolines, pyrrolidines, purines, carbazoles, indoles, phenyl indoles, 2,5-dimethylpyrroles, 3-pentafluorophenyl pyrrole, 4,5,6,7-tetrafluoroindole, 3,4-difluoropyrroles, and combinations thereof.
- 4. The process of claim 1, wherein the heterocyclic compound is substituted with one or more substituent groups selected from the group consisting of a halogen atom, and a halogen atom containing group.
- 5. The process of claim 4, wherein the halogen atom or the halogen atom group comprises chlorine, fluorine or bromine.
- 6. The process of claim 2, wherein the support material is treated with the alumoxane or the alkylaluminum compound such that the support has aluminum alkyl groups bonded thereto.
- 7. The process of claim 1, wherein the heterocyclic compound is an indole represented by:

$$X6$$
 $X7$
 $X1$
 $X2$
 $X3$
Formula (I)

wherein each of X2 to X7 is independently selected from the group consisting of hydrogen, halogen, an alkyl group, a halogenated or partially halogenated alkyl group, an aryl group, a halogenated or partially halogenated aryl group, an alkoxide group, a halogenated or partially halogenated alkoxide group, an aryloxide group, a halogenated or partially halogenated aryloxide group, an aryl substituted alkyl group, and a halogenated or partially halogenated aryl substituted alkyl group.

- 8. The process of claim 7, wherein the halogenated or partially halogenated group comprises a chlorine atom, a bromine atom or a fluorine atom.
- 9. The process of Claim 1, wherein the activator is represented one of the following formulae:

(a.)
$$(R'_X M (JY)_y)_n$$

or

(b.)
$$[((JY)_y R'_x)_n M-O-M ((R'_x (JY)_y)_n]_m$$

or

(c.)
$$(OMR'_x(JY)_y)_n$$

wherein M is a Group 13 atom;

(JY) represents a substituted or unsubstituted heterocyclic group attached to M, wherein J represents at least one heteroatom contained in the (JY) group; n is 1 or 2 in formula (a.); n is 2 in formula (b.); and n is a number from 1 to 1000 in formula (c.);

m is a number from 1 to 10;

x + y = the valence of M in formula (a.); x + y = the valence of M - 1 in formula (b.); and x + y = valence of M - 2 in formula (c.);

each R' is independently a substituted or unsubstituted alkyl group bonded to M.

- 10. The process of claim 9, wherein J is bonded to M and wherein (JY) is not perhalogenated.
- 11. The process of claim 9, wherein

M is Al or B; and

- (JY) is an substituted or unsubstituted indolyl group where the substituents are selected from hydrogen, halogen, an alkyl group, a halogenated or partially halogenated alkyl group, and aryl group, a halogenated or partially halogenated aryl group, an aryl substituted alkyl group, a halogenated or partially halogenated aryl substituted alkyl group.
- 12. The process of claim 2, wherein the support material is an Group 2, 3, 4, 5, 13 or 14 metal oxide.
- 13. The process of claim 2, wherein the support is silica.
- 14. The process of Claim 1, wherein the polymerization catalyst is a bulky ligand metallocene catalyst having the formulas:

$$\boldsymbol{L}^{A}\boldsymbol{L}^{B}\boldsymbol{M}\boldsymbol{Q}_{n}$$
 and $\boldsymbol{L}^{A}\boldsymbol{A}\boldsymbol{L}^{B}\boldsymbol{M}\boldsymbol{Q}_{n}$

wherein each of LA, LB and Q are bound to M;

each of L^A and L^B are substituted or unsubstituted cyclopentadienyl ligands or cyclopentadienyl-type ligands;

M is a Group 4, 5 or 6 transition metal;

Q is a leaving group; n is 0, 1 or 2; and

A is a divalent bridging group bound to each of L^A and L^B.

15. The process of Claim 1, wherein the polymerization process is a gas phase process.

- 16. The process of Claim 1, wherein the polymerization process is a slurry process.
- 17. The process of Claim 15, wherein the reactor temperature ranges from about 60°C to about 115°C.
- 18. The process of Claim 15, wherein the reactor pressure ranges from 100 psig (690 kPa) to about 500 psig (3448 kPa).
- 19. The process of Claim 15, wherein the reactor pressure ranges from 200 psig (1379 kPa) to about 400 psig (2759 kPa).
- 20. The catalyst system of Claim 1, wherein the catalyst system is combined in a polymerization reactor with the olefins to produce a polyolefin having a melt index ranging from 0.01 to 100 dg/min and a PDI (Mw/Mn) value of greater than 1.5 to 15.
- 21. A polymerization process comprising combining ethylene, at least one C₄ to C₁₂ α-olefin and a catalyst system comprising a polymerization catalyst, an inorganic oxide support and an activator; wherein the activator comprises a heterocyclic compound in combination with an alkylaluminum compound represented by the formula AlR₃ wherein each R is independently a substituted or unsubstituted alkyl group;
 - wherein the heterocyclic compound comprising at least one atom selected from Group 15 or 16 of the Periodic Table of Elements; and
 - wherein the polymerization catalyst is selected from bulky ligand metallocene catalysts, Group 15 atom containing polymerization catalyst compounds, and phenoxide transition metal catalyst compositions.
- 22. The catalyst system of Claim 21, wherein the support is selected from silica, fumed silica, alumina, silica-alumina, zeolites and mixtures thereof.

23. The catalyst system of Claim 21, wherein the R groups are independently selected from C_1 to C_{30} alkyls.

- 24. The catalyst system of Claim 21, wherein the alkylaluminum is selected from trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, tri-iso-octylaluminum, triphenylaluminum, and combinations thereof.
- 25. The catalyst system of Claim 21, wherein the heterocyclic compound is an indole represented by:

$$X6$$
 $X7$
 H
 $X2$
 $X5$
 $X4$
 $X3$
Formula (I)

wherein each of X2 to X7 is independently selected from the group consisting of hydrogen, halogen, an alkyl group, a halogenated or partially halogenated alkyl group, an aryl group, a halogenated or partially halogenated aryl group, an alkoxide group, a halogenated or partially halogenated alkoxide group, an aryloxide group, a halogenated or partially halogenated aryloxide group, an aryl substituted alkyl group, and a halogenated or partially halogenated aryl substituted alkyl group.

- 26. The catalyst system of Claim 25, wherein each of X2 to X7 are independently selected from hydrogen, fluorine, chlorine and bromine.
- 27. The catalyst system of Claim 21, wherein the heterocyclic compound is selected from the group consisting of pyrroles, imidazoles, pyrazoles, pyrrolines, pyrrolidines, purines, carbazoles, indoles, phenyl indoles, 2,5-dimethylpyrroles, 3-

pentafluorophenyl pyrrole, 4,5,6,7-tetrafluoroindole, 3,4-difluoropyrroles, and combinations thereof.

28. The catalyst system of Claim 21, wherein the polymerization catalyst is a bulky ligand metallocene catalyst having the formulas:

wherein each of LA, LB and Q are bound to M;

each of L^A and L^B are substituted or unsubstituted cyclopentadienyl ligands or cyclopentadienyl-type ligands;

M is a Group 4, 5 or 6 transition metal;

Q is a leaving group; n is 0, 1 or 2; and

A is a divalent bridging group bound to each of L^A and L^B.

- 29. The catalyst system of Claim 28, wherein M is titanium, zirconium or hafnium.
- 30. The catalyst system of Claim 21, further comprising an additional activator selected from aluminoxane, modified aluminoxane, tri(n-butyl)ammonium tetrakis(pentafluorophenyl)boron, trisperfluorophenylboron, trisperfluoronaphthyl boron, polyhalogenated heteroborane anions, tris(2,2',2"-nona-fluorobiphenyl) fluoroaluminate, organo-boron-aluminum compounds, dioctadecylmethylammonium-bis(tris(pentafluorophenyl)borane)benzimidazolide and combinations thereof.
- 31. The catalyst system of Claim 21, wherein the inorganic oxide support is treated with the alkylaluminum compound such that the support has aluminum alkyl groups bonded thereto.
- 32. The catalyst system of Claim 21, wherein the inorganic oxide support and alkylaluminum compound are combined prior to combining the heterocyclic compound.

- 33. The catalyst system of Claim 21, wherein the combination of the heterocyclic compound and the product of the combination of the alkylaluminum and inorganic oxide support is heated.
- 34. The catalyst system of Claim 21, wherein the catalyst system is combined in a polymerization reactor with olefins to produce a polyolefin having a melt index ranging from 0.01 to 100 dg/min and a PDI (Mw/Mn) value of greater than 1.5 to 15; wherein the olefins are ethylene and an olefin selected from C₄ to C₁₂ olefins.
- 35. A polymerization process comprising combining ethylene, at least one C₄ to C₁₂ α-olefin and a supported catalyst system; the supported catalyst system prepared by combining a heterocyclic compound with an aluminoxane or an alkylaluminum compound with a support material such that the support material contains aluminum alkyl groups bonded thereto.
- 36. The process of Claim 35, wherein the heterocyclic compound is an indole represented by:

$$X6$$
 $X7$
 H
 N
 $X2$
 $X5$
 $X4$
 $X3$
Formula (I)

wherein each of X2 to X7 is independently selected from the group consisting of hydrogen, halogen, an alkyl group, a halogenated or partially halogenated alkyl group, an aryl group, a halogenated or partially halogenated aryl group, an alkoxide group, a halogenated or partially halogenated alkoxide group, an aryloxide group, a halogenated or partially halogenated aryloxide group, an aryl substituted alkyl group, and a halogenated or partially halogenated aryloxide group.

- 37. The process of Claim 35, further comprising a support material.
- 38. The process of Claim 35, wherein the aluminum containing compound is an alumoxane or an aluminum alkyl compound represented by the formula AlR₃ wherein each R is independently a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group.
- 39. The process of Claim 35, wherein the aluminum containing compound is an alumoxane or an aluminum alkyl compound represented by the formula AlR₃ wherein each R is independently a substituted or unsubstituted alkyl group.
- 40. The process of Claim 35, wherein the heterocyclic compound is selected from the group consisting of pyrroles, imidazoles, pyrazoles, pyrrolines, pyrrolidines, purines, carbazoles, indoles, phenyl indoles, 2,5-dimethylpyrroles, 3-pentafluorophenyl pyrrole, 4,5,6,7-tetrafluoroindole, 3,4-difluoropyrroles, and combinations thereof.
- 41. The process of Claim 35, wherein the heterocyclic compound is substituted with one or more substituent groups selected from the group consisting of a halogen atom, and a halogen atom containing group.
- 42. The process of Claim 41, wherein the halogen atom or the halogen atom group comprises chlorine, fluorine or bromine.
- 43. The process of Claim 42, wherein the support material is treated with the alumoxane or the alkylaluminum compound such that the support has aluminum alkyl groups bonded thereto.